Investigation of Toxic Air Contaminants Released from Incidental Detonation of Ordnance and Explosives During Prescribed Burning of Vegetation at the Former Fort Ord, California

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INTRODUCTION

Sampling and removal activities for unexploded ordnance and explosives (OE) are required at a number of locations at the former Fort Ord prior to transfer of land by the Army to subsequent uses. The OE areas are primarily located within approximately 8,000 acres in the central and southern portion of the former base (the Inland Training Ranges), plus scattered, small areas located elsewhere on the facility.[1]

Central maritime chaparral is the dominant natural plant community in the inland ranges. In areas such as at the former Fort Ord where natural fires are suppressed by humans, the central maritime chaparral tends to form a dense canopy of intertwined stems that can become nearly impenetrable. Sampling for OE requires the use of sensors such as magnetometers that need to be swept over the ground close to the surface and are limited from effectively functioning in the dense thickets of mature chaparral. Also, the visibility of potential OE items on the ground is blocked by dense vegetation, increasing the hazard to which ordnance removal crews are exposed and making the sampling and removal process less effective.

For this reason, vegetation must be reduced or removed to provide visibility and access for OE sampling and removal activities. Mechanical (mowers, "brush hogs", chain saws, etc.) clearance of vegetation is implemented in areas of the base where it is safe do to so and where it is not prohibited by the Fort Ord Habitat Management Plan (HMP).[2] In OE areas where terrain or other safety factors make mechanical clearance impractical, or where the HMP prohibits mechanical disturbance, vegetation must be removed by prescribed burning. The prescribed burn program for the OE areas at the former Fort Ord is described in the Prescribed Burn Work Plan (PBWP) for the Former Fort Ord, Monterey County, California.[3]

Regulatory Considerations

Monterey Bay Unified Air Pollution Control District (MBUAPCD) Rule 432 "Wildland Vegetation Management Burning" regulates the use of prescribed burning for wildland vegetation management within the air district, which includes the former Fort Ord. Air pollutant emissions in smoke resulting from prescribed burning of vegetation are addressed under Rule 432 through smoke management techniques, including restricting burns to approved "burn days," prescriptions on fuel moisture content, and other procedural requirements. Criteria pollutants and toxic air contaminants (TACs) within smoke emissions from vegetation have been studied by others[4] and are not addressed in this paper.

However, MBUAPCD Rule 432 requires that the materials to be burned "shall be free from combustible impurities . . . and other material not grown at the site." Because of the possibility of incidental OE detonation during prescribed burns, the Army commissioned an investigation to assess whether incidental OE detonation would release significant quantities of TACs. For the purpose of this investigation, air pollutants are considered TACs if they are listed in MBUAPCD Rule 1000 "Permit Guidelines and Requirements for Sources Emitting Toxic Air Contaminants" or are one of 188 listed toxic air pollutants in the 1990 Clean Air Act Amendments (CAAA). Although not specifically regulated as TACs, some energetic materials (e.g., RDX and HMX) are considered TACs for this investigation because they have established human health risk values.[5]

SOURCE, NATURE, AND EXTENT OF OE AT THE FORMER FORT ORD

Generally, any type of OE used by the infantry or in support of the infantry has been or could be found on the former Fort Ord. OE found within the installation consists of conventional munitions such as large-caliber projectiles, bombs, practice bombs, grenades, practice grenades, landmines, practice landmines, rockets, detonators, blasting caps, fuses, and small arms (technically not considered an OE item, small arms are included here for completeness). Pyrotechnic OE items include flares, signals, simulators, and smoke-screen charges. Explosives, including TNT demolition charges, have also been found within the installation.[1] The most common OE items found or expected at the former Fort Ord are listed in Table 1 along with the chemical composition of their energetic materials.

Previous OE removal actions at Fort Ord suggest that OE density can vary widely in any given area of a range.[1] The highest observed density of OE with larger explosive charges (e.g., 81 mm mortars) was 16 in 60 acres (about 0.27 per acre).[6] As a worst-case assumption for this investigation, a live OE density of 10 per acre was assumed.

OE type also varies widely within the ranges. By sheer number, most live items are small arms munitions, but larger OE devices are also found. Visual surveys in the range areas suggest that the largest OE items likely to be present in quantity will be LAW rockets and 81 mm mortars.[1]

POLLUTANT PREDICTION MODEL

Overview

Of the publicly available information on military applications, a reference document by Baroody[8] and an associated computer program, POLU13L[9], developed by the Department of the Navy, Naval Surface Warfare Center, Indian Head, Maryland, provides the most comprehensive source of combustion product characterization for military ordnance. The POLU13L model has a library of over 1,400 potential combustion products that are considered in the model calculations. However, the model is limited to considering only those chemical components and additives in the explosive mixture; metals used in the casing or other structural components of OE items are expected to have little contribution to emissions and are not factored into the calculations.

The data provided by Baroody[8] for military explosives is consistent with that in USEPA AP-42[7] for conventional explosives in that the products of combustion for the most widely-used explosive mixtures are largely carbon dioxide (CO_2), carbon monoxide (CO), nitrogen (N_2), oxygen (O_2), and water (H_20). Both references suggest that only trace amounts of TACs are produced.

Application to the Former Fort Ord

A set of worst-case assumptions were developed to quantify the total net explosive weight (NEW) of OE items that may detonate during a prescribed burn. Those assumptions are:

- Maximum live OE density = 10 per acre
- Fraction of live OE items detonated during a prescribed burn = 0.5
- Maximum prescribed burn area in a single day = 1,000 acres
- All OE items are either LAW rockets (0.5 lbs. Octol/item) or 81 mm mortars (1.29 lbs. Comp B/item).

These assumptions result in an upper bound estimate of 5,000 OE items initiated during a 1,000-acre prescribed burn. If all items were LAW rockets, then the total NEW would be 2,500 lbs. Octol. If all items were 81 mm mortars, then the total NEW would be 6,450 lbs. Comp B.

The pollutant prediction model POLU13L was used in the "open detonation" mode to speciate and quantify the pollution products from these worst-case quantities of Octol and Comp B. The primary pollutant products were predicted to be N_2, O_2, CO/CO_2, and H_2O, with trace amounts of CH_4 and NH_3. None of the pollutant products predicted by the POLU13L model are regulated as TACs under either the 1990 CAAA or MBUAPCD Rule 1000.

EMPIRICAL STUDIES

Overview

A series of seven field studies funded by the U.S. Department of Defense (DOD) have been conducted to identify and quantify the pollutant species released to the air from detonating or burning energetic materials. These studies are commonly referred to as BangBox studies, because the tests were conducted inside large chambers. An August 1998 USEPA report[10] provides an analysis and summary of all the BangBox studies.

Air samples from the BangBox tests were analyzed for more than 275 individual compounds, including volatile organic compounds (VOCs), energetic and other semi-volatile organic compounds (SVOCs), particulate metals, and chlorinated dioxins and furans. Many of those compounds (103 of 108 SVOCs and over 65% of the VOCs) were never detected in any of the BangBox tests.[10] Of the 83 analytes for which emission factors are reported, most are non-hazardous compounds commonly found in ambient air.[10]

Application to the Former Fort Ord

For this investigation, the USEPA report was reviewed to identify those analytes which were associated with the types of OE at the former Fort Ord. Emission factors reported for analytes associated only with open burning of propellant wastes and other items or processes not encountered at the former Fort Ord are not considered relevant to the identification of TACs from incidental OE detonation during prescribed burns at this location.

Volatile Organic Compounds
A number of saturated VOCs (e.g., ethane, propane, butane) and unsaturated VOCs (e.g., ethylene, acetylene, and propene) were associated with detonation of OE items. These compounds, however, are environmentally benign and are not regulated as TACs.[10] The only aromatic VOCs associated with detonation of common OE items are benzene and toluene. Styrene was observed only with OE items which had polystyrene structural components. Emission factors reported for aromatic VOCs are on order of 10E-06 pounds per pound NEW.[10]

Energetic Analytes
Three energetic compounds (RDX, HMX, and PETN) were reported to be associated with OE detonations in the BangBox studies. Mean emission factors reported for energetic compounds are on order of 1E-04 pounds per pound NEW.[10]

Other Semivolatile Organic Compounds
Only one SVOC (diethylphthalate) was identified in some OE detonation samples, but only with OE items which contained pthalates (mainly some signal flares and fuzes).[10] Mean emission factors reported for diethylphthalate are on order of 1E-05 pounds per pound NEW.[10]

Dioxins And Furans
Furans were not detected above background levels in the BangBox studies. Only one dioxin isomer (OCDD) was reported and was associated only with detonation of M43A2 flares. The occurrence of OCDD likely resulted from the reaction of chloride-containing compounds and the plastic materials in the flare.[10] The mean emission factor reported for OCDD is very low, on order of 1E-09 pounds per pound NEW.[10]

Particulate Metals
Analytical results for metals in the BangBox studies were inconsistent and prevented development of valid emission factors. As a conservative approach, the report suggests that any metals within the energetic material should be assumed to be emitted to the atmosphere.[10]

Summary

Very low emission levels of a limited number of TACs were identified in the BangBox studies. Assuming even the worst-case estimates for the number of OE items that may detonate during a prescribed burn, the total mass of TAC emissions would be very small. Using the mean emission factor for benzene as an example (10E-06 pounds per pound NEW), the 6,450 pounds of Comp B detonated in the worst-case prescribed burn scenario would release on the order of only 0.06 pounds (about 29 grams) of benzene over the duration of the burn.

FIELD STUDY DESIGN

Objective and Basic Design

The primary objective of a field investigation will be to assess the presence or absence of OE-related TACs during prescribed burn activities to confirm or refine the conclusions from existing studies that no significant levels of TACs would be released. To optimize this investigation, the following design parameters are recommended:

- Prior to implementing the field sampling program, observe one or more prescribed burn events to better define the area of potential downwind smoke influence under typical "burn-day" meteorological conditions
- Schedule the field sampling to occur during a prescribed burn in an area of high OE density, so that the results of the investigation will be representative of a "worst-case" TAC emissions scenario
- Identify a target analyte list focused on OE-specific TACs to differentiate from vegetation-related TAC contributions
- Utilize field sampling methods that will facilitate rapid mobilization
- Collect downwind samples within the smoke plume as near as possible to the burn event, considering safety and access limitations
- Collect upwind samples for comparison.

Field Sampling and Analytical Methods

Aromatic Volatile Organic Compounds

Air samples for aromatic VOCs should be collected in evacuated 6-liter Summa® canisters at approximately 1 meter above ground level (agl). Each canister should be equipped with a pre-set flow controller to regulate sample collection to fill about 80 percent (4.8 liters) of the 6-liter volume over the duration of the prescribed burn event. Air samples should be analyzed for aromatic VOCs in accordance with USEPA Compendium Method TO-15 "Determination of Volatile Organic Compounds (VOCs) in Ambient Air Using Specially Prepared Canisters with Subsequent Analysis by Gas Chromatography/Mass Spectrometry."

Energetic Analytes

Air samples for energetic analytes (TNT, RDX, HMX, PETN) should be collected at approximately 1 meter agl in sorbent sampling media such as OSHA Versatile Sampler (OVS) tubes. Battery-operated low-flow sample pumps may be used to draw air samples into the OVS tubes over the duration of the prescribed burn event. Air samples should be analyzed for the target list of energetic analytes via High Performance Liquid Chromatography Mass Spectroscopy (LCMS).

Particulate Metals

Air samples for particulate metals should be collected at approximately 1 meter agl on 47 mm Teflon filter media. Battery-operated low-flow sample pumps may be used to draw air samples onto the filter media over the duration of the prescribed burn event. Air samples should be analyzed via x-ray fluorescence (XRF) for the following target list of particulate metals which are known to be present as chemical additives or components of some OE items:

- Aluminum
- Antimony
- Barium
- Beryllium
- Cadmium
- Chromium (total)
- Copper
- Lead
- Nickel
- Titanium
- Zinc

Other Compounds

Dioxins, furans, and non-energetic SVOCs are not considered crucial to a field investigation because these compounds were not generally associated with OE detonation in the BangBox tests. Their presence or absence in downwind samples would not be conclusive evidence of TAC emissions from OE detonation.

Quality Control Samples

One downwind sample location should be used to collect duplicate samples (one for each different media/analytical method) to be submitted blind along with the primary sample to the respective laboratories. One unexposed set of field blanks should also be submitted blind for the energetic analytes (OVS tubes) and particulate metals (filter samples). One Summa® canister should be prepared as a field blank by allowing the canister to fill through a conditioned high-capacity charcoal sorbent trap. Each laboratory should also be requested to run and report method blanks and surrogate spikes consistent with the analytical methods used.

CONCLUSIONS

A pollutant prediction model was applied to worst-case estimates of OE type, density of occurrence, and fraction initiated by heat to estimate total pollutant emissions for a maximum (1,000-acre) prescribed burn scenario at the former Fort Ord. Results of the model indicate that no TACs would be expected to be released. These model results would also apply to OE sites at other military installations where OE density, composition, and size of the burn area are similar.

Analytical results from a series of BangBox emission tests were examined and applied to the common types of OE items at the former Fort Ord. These results suggest that several TACs may be released from incidental OE detonations during prescribed burns, but emission rates of these TACs are reported to be very low. These emission estimates are also applicable to prescribed burns at other military installations with similar conditions of OE density and composition.

Although very applicable, both of these previous studies have limitations which warrant further investigation. Most notably, the pollutant prediction model does not address the possible emission contribution of metals from OE structural components. It also fails to predict emissions of several TACs which were observed at low levels during BangBox tests of common OE items. The results of the BangBox tests were useful in eliminating many TACs from the list of possible byproducts of OE detonation, but some results, such as for particulate metals, were inconclusive.

A field investigation was designed to address these limitations and to confirm or refine the conclusion that significant amounts of TACs are not expected from incidental OE detonation during prescribed burns at the former Fort Ord or other similar locations. A target analyte list was developed that will optimize the investigation for detection of OE-related TACs.

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Table 1. Most Prevalent OE Items at the Former Fort Ord, California, and their Primary Energetic Components

Item Description[1]	**Primary Energetic Component(s)** [2]
Dragon Rocket, M223	Octol 70/30 (HMX[(a)]/TNT[(b)])
106 mm, M344A1	Comp B (RDX[(c)]/TNT)
3.5 inch Rocket, M28	Comp B (RDX/TNT)
84 mm, M136 (AT-4)	Comp B (RDX/TNT)
81 mm M43A1	Comp B (RDX/TNT)
66 mm TPA, M74	Triethylaluminum
66 mm, M72 (LAW Rocket)	Octol 70/30 (HMX/TNT)
2.36 inch Rocket, M6A1	50/50 Pentolite (TNT/ PETN[(d)])
60 mm, M49A2	Comp B (RDX/TNT)
M9 Rifle Grenade	Comp B (RDX/TNT)
57 mm, M306A1	Comp B (RDX/TNT)
40 mm, M381	Comp B (RDX/TNT)
40 mm, M677 (Mk19)	Cyclotol 70/30 (RDX/TNT)
35 mm Subcal, M73	Flash Composition [(e)]
22 mm Subcal for 81 mm mortar, M744	Smoke Charge [(f)]
Small arms (7.62 mm, 5.56 mm, 50 and 30 cal)[3]	Nitrocellulose, Nitroglycerin
Pyrotechnics (misc. flares and signals)	Illuminant Composition [(g)]

[1]Source: Reference 1.

[2]Source: Reference 11.

[3]Small arms are technically not OE items, but are included here for completeness.

[(a)] HMX (1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane)

[(b)] TNT (2,4,6 trinitrotoluene)

[(c)] RDX (1,3,5-trinitro-1,3,5-triazacyclohexane)

[(d)] PETN (pentaerythrite tetranitrate)

[(e)] Flash Composition: Potassium Perchlorate, Flaked Aluminum, Sulfur

[(f)] Smoke Charge: Potassium Perchlorate, Aluminum Powder

[(g)] Illuminant Composition (typical): Aluminum or Magnesium Powder, Sodium or Barium Nitrate